AFRL-SR-BL-TR-98-

0208

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (*Leave blank*)

2. REPORT DATE
February 15, 1998

3. REPORT TYPE AND DATES COVERED
Final Technical, 6/15/94-9/14/97

4. TITLE AND SUBTITLE
The Materials Science and Mathematics of Block Copolymers

5. FUNDING NUMBERS
F49620-94-1-0357
3484/XS
61103D

6. AUTHOR(S)
Edwin L. Thomas

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, MA 02139

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Dr. Charles Lee
AFOSR/NC
110 Duncan Avenue, Suite B115
Bolling AFB DC 20332-0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

19980225 060

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

This project focused on the fundamentals of microstructural control of polymer materials for three-dimensional nanocomposites. Our recent discovery of the double gyroid (DG) microdomain structure in a polystyrene-polyisoprene diblock copolymer (*Macromolecules* 27, 4063 (1994)) opened the possibility for exploiting this new tricontinuous structure for physical properties. Two possible applications we envisioned were for tough thermoplastic elastomers and for nanoporous membranes. In the past three years, we demonstrated the attainment of this specific tricontinuous triply periodic microdomain structure in two different triblock copolymers for the first time, through targeted composition and chain architecture. Additionally we have collaborated with mathematicians to model the complex DG structure employing level set functions and to develop a software application program for producing 2D projections of the 3D microdomain structure for comparison to TEM images. Two polystyrene-polyisoprene ABA triblock samples which have the DG structure were synthesized and their large strain deformation behavior investigated using a combination of transmission electron microscopy (TEM) and in situ synchrotron small angle x-ray scattering (SAXS). Additionally, triblock DG samples based on poly(pentamethyl disilylstyrene)-polyisoprene were synthesized and successfully converted into nanoporous materials via ozonolysis etching of the polyisoprene networks.

14. SUBJECT TERMS
nanocomposites; double gyroid; insitu synchrotron SAXS; deformation behavior; thermoplastic elastomers; level surfaces

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclassified	unclassified	unclassified	SAR

Air Force Final Technical Report
F49620-94-1-0357
AASERT

The Materials Science and Mathematics of Block Copolymers
June 15, 1994 - September 15, 1997

Edwin L. Thomas
Department of Materials Science and Engineering
MIT
Cambridge, MA 02139

Overview of Project

This project focused on the fundamentals of microstructural control of polymer materials for three-dimensional nanocomposites. Our recent discovery of the double gyroid (DG) microdomain structure in a polystyrene-polyisoprene diblock copolymer (*Macromolecules* 27, 4063 (1994)) opened the possibility for exploiting this new tricontinuous structure for physical properties. Two possible applications we envisioned were for tough thermoplastic elastomers and for nanoporous membranes. In the past three years, we demonstrated the attainment of this specific tricontinuous triply periodic microdomain structure in two different triblock copolymers for the first time, through targeted composition and chain architecture. Additionally we have collaborated with mathematicians to model the complex DG structure employing level set functions and to develop a software application program for producing 2D projections of the 3D microdomain structure for comparison to TEM images. Two polystyrene-polyisoprene ABA triblock samples which have the DG structure were synthesized and their large strain deformation behavior investigated using a combination of transmission electron microscopy (TEM) and in situ synchrotron small angle x-ray scattering (SAXS). Additionally, triblock DG samples based on poly(pentamethyl disilylstyrene)-polyisoprene were synthesized and successfully converted into nanoporous materials via ozonolysis etching of the polyisoprene networks.

Mechanical Behavior

Two triblock copolymers of the ABA type, where A is polystyrene (PS) and B polyisoprene (PI) were anionically synthesized with the volume fraction of the minority component, PS or PI, at approximately 1/3. Tricontinuous cubic microdomain morphologies, already found in diblock and star block copolymers with the same composition range, were observed for the first time in the case of linear triblock copolymers. The two ABA triblocks are on

opposite sides of the phase diagram, which signifies that both the A endblocks and the B midblock are capable of forming the double interconnected DG network structure. Investigation of the morphology was done via birefringence, small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). Birefringence measurements showed each triblock structure to have isotropic optical properties. The characteristic ratio of the observed Bragg peaks q_2/q_1, was approximately $\sqrt{4}/\sqrt{3}$ for each sample indicating a set of eight possible space groups. Since the two triblocks have essentially complementary structures (PS = 0.32 in one and PI = 0.36 in the other) the TEM images of OsO_4 stained thin sections are complementary and the diffraction patterns of the images approximately equal according to Babinet's principle. Examination of high symmetry projections demonstrated p6mm, p4mm and c2mm symmetry present in the TEM images. Comparison with the <111>, <100> and <110> projections of the 8 cubic space groups satisfying the SAXS data eliminated all but the $Fm\bar{3}m$ and the $Ia\bar{3}d$ groups as possible structures. Due to the observed connectivity of the structure, the $Fm\bar{3}m$ structure could be eliminated by inspection of possible network structures and the resultant symmetries. Computer simulations of a model structure (double gyroid) based on level surfaces with $Ia\bar{3}d$ symmetry and their Fourier transforms showed excellent agreement with the high symmetry projections and their respective optical transforms. This work was published in Macromolecules (1). Once triblock DG copolymers were available we investigated their large strain mechanical properties.

Quiescently cast samples exhibit the DG structure with Ia3d space group. Roll-casting of the PS/PI/PS triblocks however, results in a transformation of the structure from the cubic phase to a cylindrical phase with the [0001] direction of the cylindrical phase aligned along the roll-cast flow direction. Fortunately, upon annealing, the cylindrical phase converts to the DG with a near single-crystal texture. The samples are well ordered and highly anisotropic, the DG sample morphology exhibiting 8 equatorial reflections in the SAXS patterns. The large-strain deformation behavior of both isotropic films and highly oriented films were studied via synchrotron SAXS (2, 3). The oriented samples were stretched in the [111] direction. For deformation along the [111] direction, the stress-strain curve exhibits a yield point which is due to necking phenomenon. The character of the 2D SAXS patterns changes suddenly from discrete Bragg spots up to yield (10-15% strain) to patterns exhibiting lobes and streaks, which thereafter evolve with little change up to deformations of 650%. During unloading, the return of Bragg-like spots is observed at 250-200% strain; a new pattern, dubbed the "tie-fighter", develops and remains at zero load with 75% residual strain. The unloaded structure completely heals upon annealing; SAXS patterns for the annealed structure are nearly identical to the original, implying that the interpenetrating PS networks are not destroyed when taken to high deformation and can reform into their original oriented state upon relaxation and further thermal treatment. Samples

deformed to different strains and fixed via high energy electron crosslinking were observed with TEM to determine real-space morphology. The correlation of the FFT patterns of the TEM images with the SAXS patterns was excellent. Both SAXS and TEM data were used to infer deformation mechanisms of the microstructure (3).

Morphological Control Via Architecture

Variation in chain architecture should influence the actual geometry of the microdomains. In order to try to induce a new microdomain morphology via architecture we chose a 50/50 A/B composition since at this composition in the strong segregation limit, the classical lamellar morphology dominates the phase diagram. To this end, Prof N. Hadjichristidis (U Athens) designed and synthesized multiblock copolymers containing several blocks of different molecular weight, but remaining symmetric in overall composition. The copolymers synthesized were linear tetrablocks and inverse star diblocks (called miktoarm stars: mixed arm stars). An architecturally induced morphological transition from the normal lamellar to a tricontinuous cubic structure occurred for the most asymmetric arm copolymer (4). The transformation of a flat IMDS structure to a highly curved IMDS of the tricontinuous cubic structure was proposed to result from the need to avoid overcrowding of looped-interior blocks and/or to avoid the extreme stretching of the bridged-interior blocks in the star copolymer.

Further studies on the influence of chain architecture on the microdomain morphology were conducted on a series of miktoarm star block copolymers of the $(PS\text{-}b\text{-}PI)_n$ PS type where $n = 2, 3$ and a bridged block copolymer of the $(PS\text{-}b\text{-}PI)_3PS(PI\text{-}b\text{-}PS)_3$ type (5). The initial volume fraction of PS (ϕ_{PS}) for each copolymer was 0.51-0.56, leading to the observation of a lamellar morphology. The transition from lamellar domains to another morphology was studied by preparing binary blends of the copolymers with homopolystyrene (hPS) of low molecular weight ($M_w = 10200$ kg/mol) in order to be easily absorbed in the PS phase. A behavior similar to diblock and triblock lamellae to cylinders when $\phi_{PS} = 0.69$, *without* the observation of cubic microdomains. Such a behavior is explained by the complex architecture of the copolymers and the molecular weights of the PS and PI blocks.

Mathematical Modeling of the IMDS

In our on-going collaboration with mathematician Hoffman (Berkeley) we have developed the concept of treating the interface between two block copolymer components as a mathematical surface (called the Intermaterial Dividing Surface, IMDS) and characterizing this surface via its mean and Gaussian curvatures and the area per block copolymer. This approach has been extremely useful in enabling a broad understanding of a whole host of block copolymer and

homopolymer/block copolymer systems. Many observations of microdomains in block copolymers have shown that the IMDS is approximately constant mean curvature (CMC). The classical sphere, cylinder and lamellar structures are of course constant curvature structures. The two triply periodic tricontinuous structures, the double diamond and the double gyroid, are well represented by IMDS from CMC families based on the D and G minimal surfaces respectively. Indeed a CMC surface fulfills the mathematical requirement that the area of the interface be minimized at fixed volume fraction. However, the free energy problem requires not only minimization of the interfacial energy, but maximization of the chain entropy. This latter constraint can cause deviations from a IMDS with CMC. Non-CMC behavior is expected when the geometry of the microdomains is such that a block is subjected to large variations in the average domain thickness. In such cases, the entropic penalty of chain deformation outweighs the cost of additional interfacial energy so that the IMDS is perturbed to yield a more uniform distribution of domain thickness. The need has arisen to readily model families of surfaces which can serve as candidate surfaces for rapid calculations in TEM/sim and also for the simulation of SAXS patterns. For this purpose we have undertaken to study *level surface* models. Level surfaces are functions of points which satisfy the equation $F(x,y,z) = t$ where t is a constant. To construct such surfaces we start with the symmetries of a chosen space group and construct the function by a Fourier series coming from the particular allowed reflections of the space group (6). Except for special values of t, where singularities may occur, the surfaces are smooth and non-self-intersecting. For example, they make quite good representations of triply periodic CMC surfaces of the DG microdomain morphology. The software application program TEMsim is available for free downloading at http://www.msri.org/computing/JTHapps/index.htmd.

Polymers for Nanoporous Membranes

A block copolymer with one block easily etched by an oxygen plasma and another silicon containing block may form a periodic S_iO_x structure. We synthesized of silicon containing triblock copolymers of the type ABA and BAB where A is polyisoprene (PI) and B is poly(pentamethyldisilylstyrene) (PMDSS) respectively (7). It was found that the PMDSS behaves very similarly to styrene in that it could be polymerized to reasonably high molecular weights and targeted compositions were obtained. The molecular weight of the ABA polymer was 28K-98K-27K which corresponded to 34 wt% of PI, while that for the BAB polymer was 50K-250K-50K and corresponded to 16 wt% of PMDSS. The morphology of the PMDSS-PI block copolymers were characterized by SAXS and optical diffraction. From TEM micrographs, the ABA polymer was shown to exhibit the DG cubic morphology while the BAB polymer exhibited a spherical morphology. This double gyroid morphology is the first to be reported in a silicon containing

block copolymer and consists of a matrix of PMDSS and a network of PI. Due to the etch selectivity of the PMDSS block in an oxygen plasma relative to the PI block, it should be possible to remove the network through reactive ion etching and convert the PMDSS to S_iO_x. Preliminary ozonolysis, demonstrates the selective removal of the PI channels yielding a nanoporous PMPSS material.

Personnel Supported

Graduate Students
V. Chan, Department of Materials Science and Engineering, MIT
B. Dair, Department of Materials Science and Engineering, MIT

Undergraduate Student
C. Lambert, Department of Mathematics, MIT

Collaborators

N. Hadjichristidis, University of Athens
A. Avgeropoulos, University of Athens
Y. Tselikas, University of Athens
D. Hoffman, MSRI, Berkeley
R.D. Miller, IBM, Almaden
V.Y. Lee, IBM, Almaden
D. Ngo, IBM, Almaden
M. Capel, Brookhaven National Labs

L. Radzilowski, MIT
R. Lescanec, MIY
M. Wohlgemuth, MIT & Freiberg, Germany
C. Honeker, MIT

Papers Published/Submitted

1. A. Avgeropoulos, B.J. Dair, N. Hadjichristidis and E.L. Thomas, *Macromolecules*, 30, 5634-5642 (1997). "The Tricontinuous Double Gyroid Cubic Phase in Triblock Copolymers of the ABA-Type."

2. B.J. Dair, E. Prasman, E.L. Thomas and M. Capel, *Deformation Yield and Fracture Conference* 565-569 (1997), "Deformation Behavior of Cubic Block Copolymer Morphologies with Discrete or Tricontinuous Glassy Microdomains."

3. B.J. Dair, E.L. Thomas, M.S. Capel, A. Avgeropoulos and N. Hadjichristidis, J. Mat. Sci., to be submitted, "Deformation Behavior of the Double Gyroid Phase in Triblock Copolymers."

4. Y. Tselikas, N. Hadjichristidis, R. L. Lescanec, C. C. Honeker, and M. Wohlgemuth and E. L. Thomas, *Macromolecules*, 29, 3390-3396 (1996) "Architecturally Induced Tricontinuous Cubic Morphology in Compositionally Symmetric Miktoarm Star Block Copolymers."

5. A. Avgeropoulos, N. Hadjichristidis, B.J. Dair and E.L. Thomas, to be submitted, "Morphological Behavior of Miktoarm Star Polystyrene-polyisoprene Block Copolymers and their Blends with Homopolystyrene."

6. C. A. Lambert and L.H. Radzilowski, and E. L. Thomas, *Phil. Trans. R. Soc., London*, A, 354, 1-16 (1996) "Level Surfaces as Models for Cubic Tricontinuous Block Copolymer Morphologies."

7. A. Avgeropoulos and V. Chan, V.Y. Lee, D. Ngo, R.D. Miller, N. Hadjichristidis, E.L. Thomas, Chemistry of Materials, accepted, January 1998, "Synthesis of Linear Poly(isoprene) Poly(pentamethyldisilylstyrene)Triblock Copolymers for Nanolithographic Applications."